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THE EFFECT OF ACTIVATION ENERGY ON TUBULAR REACTOR MULTIPLICITY

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Robert F. Heinemann and Aubrey B. Poore*

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ABSTRACT

The effect of activation energy on the steady state solutions exhibited by the nonadiabatic tubular reactor is investigated by applying numerical bifurcation techniques to the model equations. As the activation energy is increased, the solution branch becomes more complex and finally evolves into a multiplicity pattern with regions of one, three, five and seven solutions. Only the states of lowest and highest temperature are found to be stable. This work confirms recent results using large activation energy asymptotics and links these results to previous numerical studies of reactor multiplicity employing low to moderate values of activation energy.

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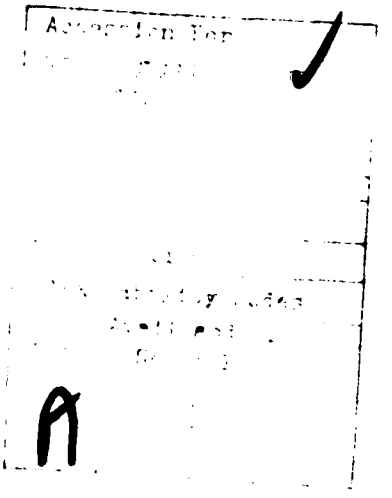
SIGNIFICANCE AND EXPLANATION

The solutions exhibited by chemical reactor models not only predict performance but in the case of multiple steady states also elucidate reactor dynamics which arise due to transitions between stable solutions. We trace the response curves for the tubular reactor with an $A \rightarrow B$ reaction as the activation energy γ (the model parameter which controls the effect of temperature on reaction rate) is increased from low to extremely large values. These curves become quite complex as γ is assigned large values, however the dynamic capabilities of reactor do not increase with γ since only the solutions of highest and lowest temperature are stable.



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THE EFFECT OF ACTIVATION ENERGY ON TUBULAR REACTOR MULTIPLICITY

Robert F. Heinemann and Aubrey B. Poore*

INTRODUCTION

The existence of multiple steady states in the tubular reactor with axial mixing was first illustrated by the numerical computations of van Heerden (1). Many papers have followed his lead by theoretically and numerically investigating the uniqueness, stability, sensitivity, and structure of the solutions exhibited by this fundamental type of reactor. Theoretical examinations have centered around the determination of criteria for uniqueness and stability in terms of the model parameters. Several analytical methods have been employed: first-order lumping, Liaponov functions, comparison theorems, and fixed-point analyses. Their application has shown that in general the solutions exhibited by the reactor are unique for sufficiently large Peclet numbers, large heat transfer coefficients, small reactor length, and small Damkohler number. These conclusions are given in the reviews of Varma and Aris (2) and Schmitz (3) and in the works of Hlavacek and Hofmann (4), Luss et al. (5-7), Varma and Amundson (8-10) and McGowin and Perlmutter (11).

Multiple solutions have been numerically studied by applying variations of the shooting and collocation methods to the reactor equations using model parameters well outside the range given by the uniqueness criteria in the above references. The investigations of Varma and Amundson (12-13), Hlavacek (14-16), McGowin and Perlmutter (17), and Jensen and Ray (18) have determined

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the existence and stability of one, three, and five steady state solutions and have examined the effect of the system parameters on the range of multiplicity. Although sustained oscillations were also demonstrated in the nonadiabatic case, the above studies were primarily directed toward the multiplicity problem and the associated hysteresis and jump phenomena which occur at transitions between stable operating states in the reactor. Kapila and Poore (19) have recently classified the steady state solutions for all system parameters in the asymptotic limit of large activation energy. These perturbational methods show that the reactor may in fact exhibit seven steady states for higher activation energies.

The goal of this work is to show how the one, three and five steady states, which were studied extensively in the seventies, evolve into the newly discovered seven steady states. The present study then confirms the work of Kapila and Poore and ties it to the work of the previous investigators.

MATHEMATICAL MODEL AND NUMERICAL TECHNIQUES

The steady state conservation equations describing an $A \rightarrow B$ reaction in the nonadiabatic tubular reactor with axial mixing are written below in dimensionless form

$$\frac{1}{Pe_m}\frac{d^2c}{dx^2} - \frac{dc}{dx} - Dce^{\gamma-\gamma/T} = 0$$

$$\frac{1}{Pe_h}\frac{d^2T}{dx^2} - \frac{dT}{dx} - \beta(T - T_c) + BDce^{\gamma-\gamma/T} = 0$$

These equations are subject to the following boundary conditions

$$\frac{\partial c}{\partial x} = Pe_m(c - 1) \qquad \text{at} \quad x = 0$$

$$\frac{\partial T}{\partial x} = Pe_h(T - 1) \qquad \text{at} \quad x = 0$$

$$\frac{\partial c}{\partial x} = \frac{\partial T}{\partial x} = 0 \qquad \text{at} \quad x = 1$$

The variables c and T represent the dimensionless concentration of reactant A and reactor temperature. The parameters $Pe_m, Pe_h, \beta, T_c, B, D,$ and γ denote respectively the Peclet number for mass transfer, the Peclet number for heat transfer, the heat transfer coefficient, the coolant temperature, the heat of reaction, the Damkohler number and the activation energy.

We investigate reactor multiplicity by computing the steady state solutions of the above model as the Damkohler number is varied. The boundary value problem is discretized by a fourth-order finite difference scheme due to Stepleman (20), and the resulting nonlinear algebraic equations are solved by Keller's arclength modification of the Euler-Newton continuation procedure (21). Since these methods are discussed in the literature (22, 23), we forego any further discussion of these techniques. The stability of the steady states is determined by computing the eigenvalues of the discretized system via the QZ algorithm.

MULTIPLICITY PATTERNS

The results of our computations are represented on response curves which represent the maximum reactor temperature (the largest value of T found on the computed temperature profile) plotted against the Damkohler number. We examine the effect of the activation energy on the reactor multiplicity by tracing the response curve as γ varies from 25 to 225 while the remaining parameters are fixed at $Pe_m = Pe_h = 1.0$, $\beta = 4.0$, $B = 0.5$ and $T_c = 1.0$.

This set of parameters falls into the range for which seven steady states are predicted by the analysis of Kapila and Poore. More specifically, let $r_{\pm} = \frac{1}{2} Pe_h[1 \pm (1 + 4\beta/Pe_h)^{1/2}]$ and $\alpha(\beta,Pe_h) = (\exp(r_+) - \exp(r_-))/(r_+\exp(r_+) - r_-\exp(r_-))$. If β_c denotes the value of β for which $\beta\alpha(\beta,Pe_h) = 1$, then in the asymptotic limit of large activation energy, there exists for some range of the Damkohler number, three solutions for $\beta = 0$, five solutions for $0 < \beta < \beta_c$ and seven solutions for $\beta > \beta_c$(19). (For $Pe_h = 0$, β_c is approximately 1.4 while for Pe_h larger than 4, β_c is slightly larger than $1 + Pe_h$.) Although we present the transition to seven steady states for only one set of parameters, the results are quite similar for other sets satisfying the above criteria.

In Figure 1, we show that the reactor model yields a branch of unique, stable steady state solutions for $\gamma = 25$. As γ is increased to 40, a region of three solutions appears for a very narrow range of the Damkohler number. A close examination of this solution branch indicates that all three solutions may be unstable since exchanges in stability do not occur at the static bifurcation points but rather at the Hopf bifurcation points where periodic solutions bifurcate from the solution branch and surround the unstable steady states (24, 19).

The remaining solution branches in Figure 1 all exhibit five solutions over some range of D. An inner loop, which grows as γ is increased, appears on the intermediate section of the usual S-shaped curve, and this loop gives rise to the five steady states. For each of these solution branches the first exchange of stability occurs at the lower limit point, and all of the intermediate solutions are unstable until a Hopf bifurcation point is encountered above and to the right of the upper limit point. We also note that the $\gamma = 75$ branch has the identical shape of the multiplicity pattern

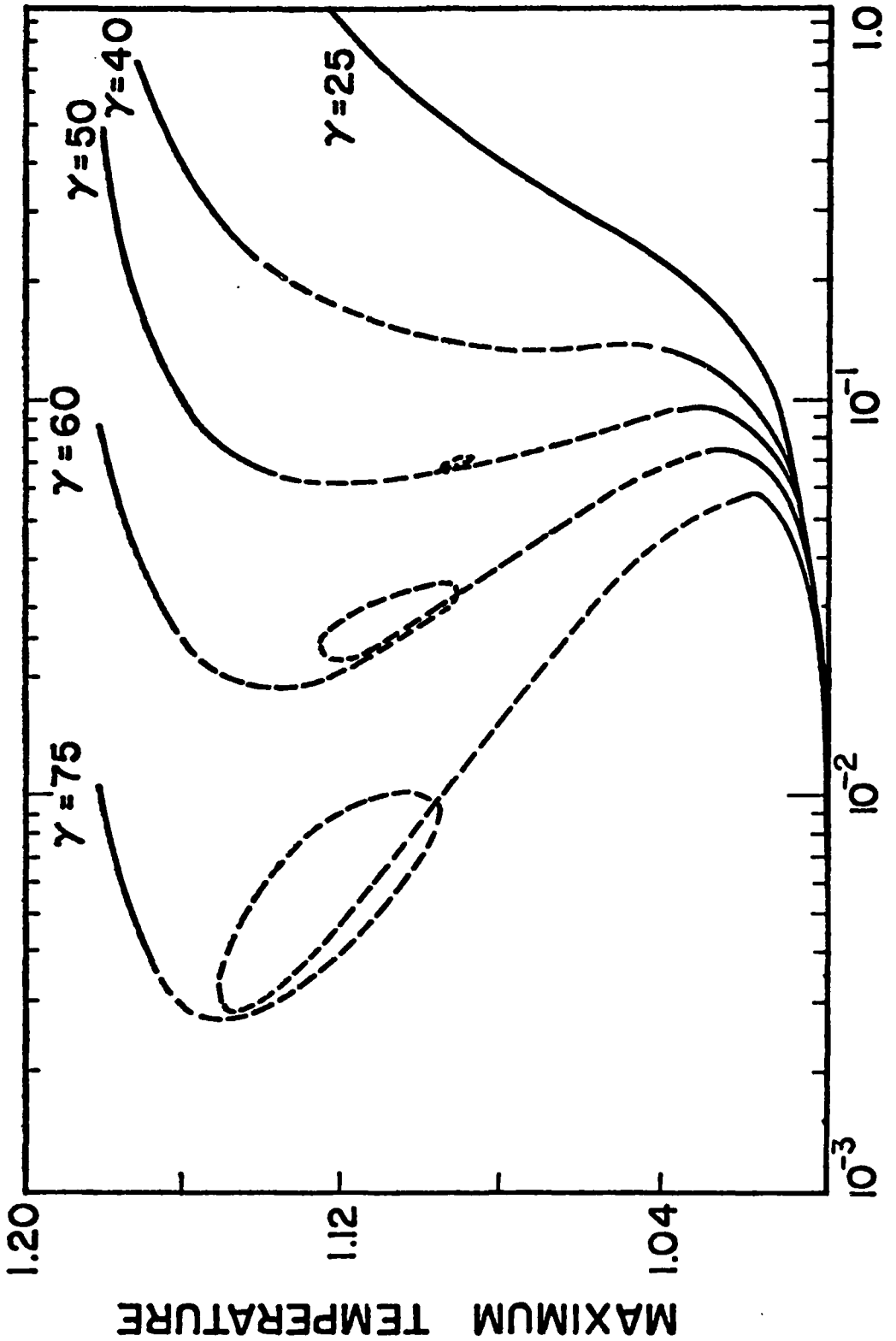

Figure 1. The Effect of Activation Energy on Reactor Multiplicity: Transition from One to Five Solutions.

predicted by Kapila and Poore (19) for $0 < \beta < \beta_c$. (Our computations with $Pe = 1.0$, $\beta = 1.0$, $B = 0.5$ and $\gamma = 100$ confirm the Kapila and Poore predictions for $0 < \beta < \beta_c$ but are not presented here because of their similarity with $\gamma = 75$ results of Figure 1.)

In Figure 2, γ is increased to 100 and 125, and seven solutions appear in both cases when two limit points arise along the lower, right-hand portion of the inner loop. This region is barely detectable for $\gamma = 100$ and is slightly broadened for $\gamma = 125$ as this S shaped perturbation of the inner loop is more clearly defined. The lower two solutions on this perturbation correspond to the additional solutions established by Kapila and Poore. The stability results for the branches in Figure 2 are the same as those for $\gamma = 75$, where all the solutions except the lowest and highest temperature states are unstable.

The exclusion of the lower limit points ($D = 0.042$ for $\gamma = 100$ and $D = 0.032$ for $\gamma = 125$) from Figure 2 indicates the effect of large γ on the location of the multiplicity regions. It is clear from the definition of D (D is proportional to $e^{-\gamma}$ (3).) that increasing γ to such large values must shift the solution branch rather dramatically to the left.

The result of increasing γ to 225 is illustrated in Figure 3 where seven solutions are shown for a narrow range of D ($7.0 \times 10^{-10} < D < 1.35 \times 10^{-9}$) and five solutions are shown over a relatively wide range ($5.0 \times 10^{-12} < D < 5.5 \times 10^{-6}$) as the perturbation on the inner loop becomes quite exaggerated. The maximum temperature of the newly discovered solutions becomes identical along the lower portion of the perturbation, but the locations of the maximums occur at different points along the reactor. The solution branch for this extremely large value of γ

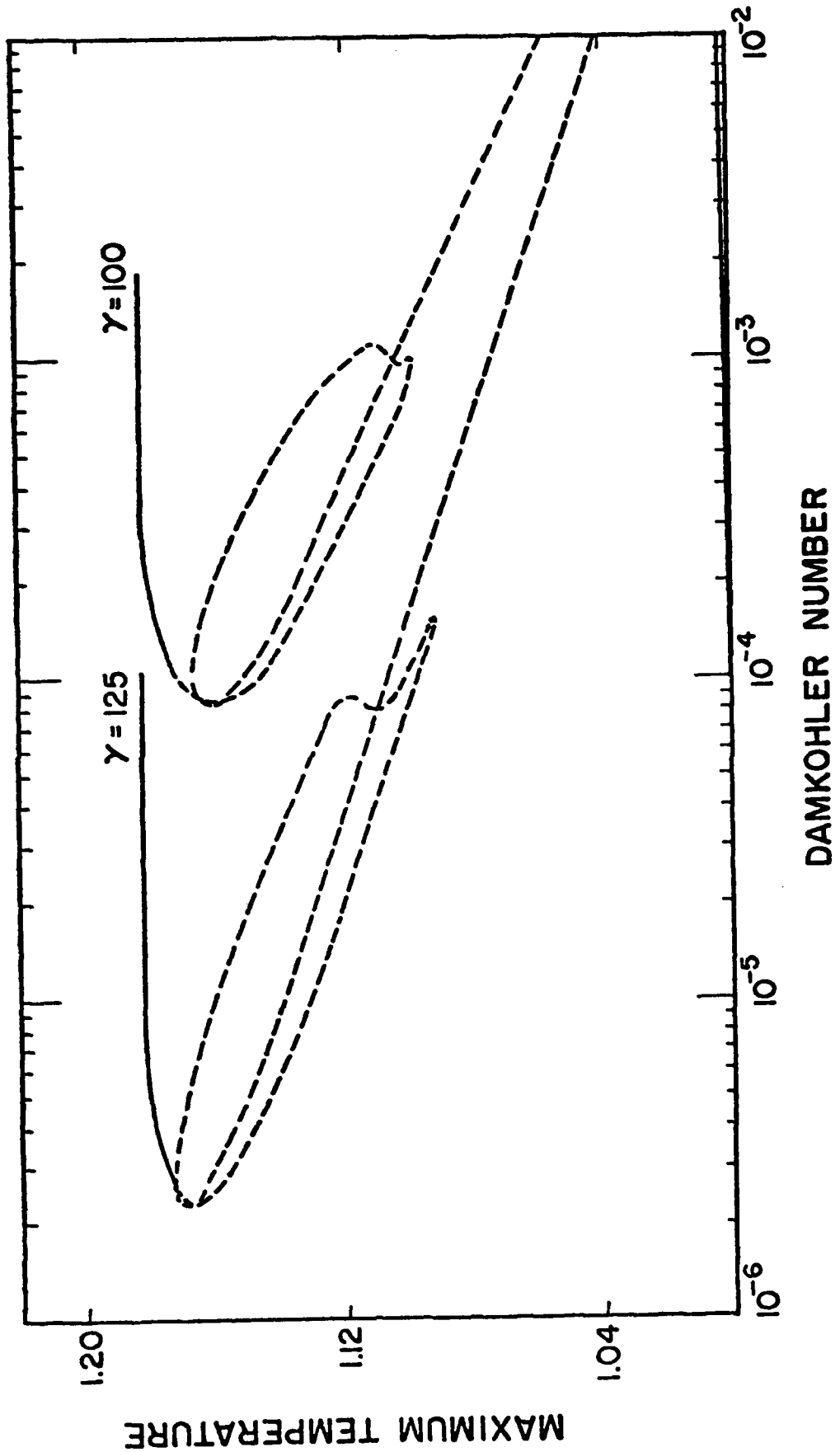

Figure 2. Solution Branches Exhibiting 1-3-5-7-5-3-1 Multiplicity.

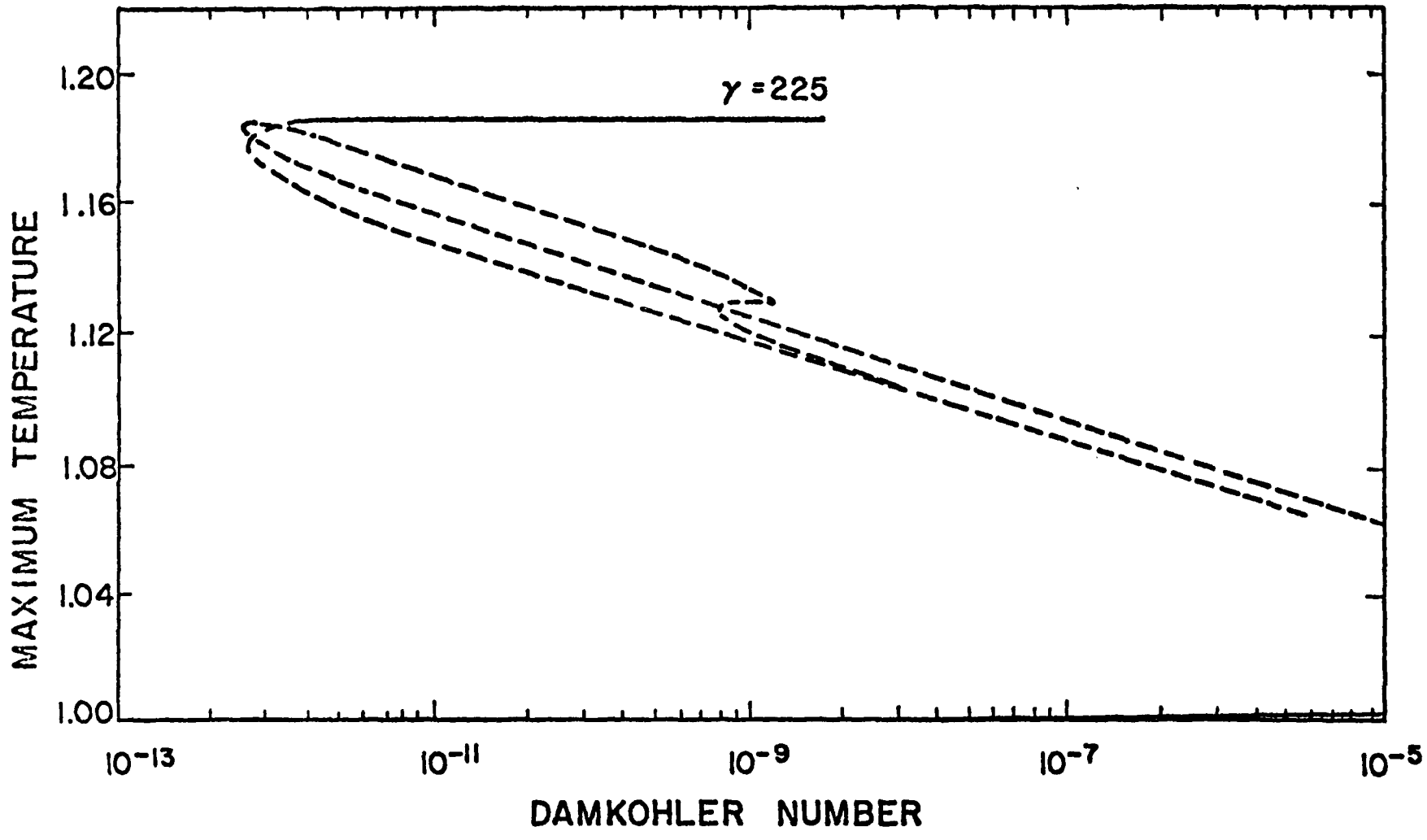

Figure 3. Response Diagram for Extremely Large Activation Energy: Confirmation of Asymptotic Results in [19].

shows excellent agreement with the asymptotic results for large activation energy presented by Kapila and Poore [19].

CONCLUSIONS

We have illustrated the effects of activation energy on the steady state multiplicity of the tubular reactor. As the activation energy increases, the solution branch becomes more complex and evolves into a pattern of seven solutions of which only two (states of lowest and highest temperature) are stable.

REFERENCES

1. Van Heerden, C., Ind. Eng. Chem. 1958 8 133.
2. Varma, A. and Aris, R., in Chemical Reactor Theory, eds. N. R. Amundson and L. Lapidus, Prentice-Hall, New Jersey, 1977.
3. Schmitz, R., Adv. Chem. Ser. 1975 148 156.
4. Hlavacek, V. and Hoffmann, H., Chem. Engng. Sci. 1970 25 173.
5. Luss, D., Chem. Engng. Sci. 1971 26 1713.
6. Luss, D. and Amundson, N. R., Can. J. Chem. Eng. 1967 45 341.
7. Luss, D. and Amundson, N. R., Chem. Engng. Sci. 1967 22 253.
8. Varma, A. and Amundson, N. R., Chem. Engng. Sci. 1972 27 907.
9. Varma, A. and Amundson, N. R., Can. J. Chem. Eng. 1972 50 470.
10. Varma, A. and Amundson, N. R., Can. J. Chem. Eng. 1973 51 206.
11. McGowin, C. R. and Perlmutter, D. D., Chem. Eng. J. 1971 2 125.
12. Varma, A. and Amundson, N. R., Can. J. Chem. Eng. 1973 51 459.
13. Varma, A. and Amundson, N. R., Can. J. Chem. Eng. 1974 52 580
14. Hlavacek, V. and Hoffmann, H., Chem. Engng. Sci. 1970 25 187.
15. Hlavacek, V. and Hoffmann, H., Chem. Engng. Sci. 1970 25 1517.

16. Hlavacek, V., Hoffmann, H. and Kubicek, M., Chem. Engng. Sci. 1971 26 1629.

17. McGowin, C. R. and Perlmutter, D. D., AICHE J. 1971 17 831.

18. Jensen, K. F. and Ray, W. H., Submitted for publication, 1980.

19. Kapila, A. and Poore, A. B., Submitted for publication, 1980.

20. Stepleman, R. S., Math. Comp. 1976 30 92.

21. Keller, H. B., in Applications of Bifurcation Theory, ed. P. H. Rabinowitz, Academic Press, New York, 1977.

22. Heinemann, R. F., Overholser, K. A. and Reddien, G. W., Chem. Engng. Sci. 833 34 1979.

23. Heinemann, R. F., Overholser, K. A. and Reddien, G. W., AICHE J. 725 26 1980.

24. Heinemann, R. F. and Poore, A. B., Submitted for publication, 1980.

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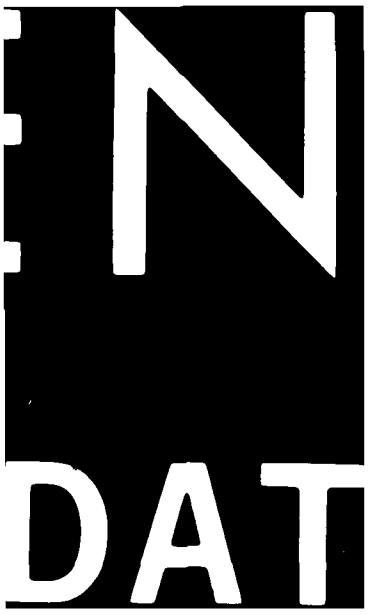
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